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Radionuclide Data Analysis of Marine Subsistence Food from Amchitka and Adjoining Areas

Mark Baskaran Ph.D.
Department of Geology
Wayne State University
Detroit, Michigan

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1. Introduction:

Derivation of dose estimates from subsistence food such as fish require that the concentrations of radionuclide are precisely known. The safety of subsistence food and the ecosystem in areas adjoining Amchitka requires that the radionuclide concentration of anthropogenic radionuclides, potentially released from the three nuclear tests between 1965 and 1971 at Amchitka Island in the central Aleutian Archipelago, in subsistence food. The total yield of these detonations (6.08 million tons) is estimated to be about 15% of the total yield of all US underground nuclear explosions {Long shot: 80 kton at 690 m below the island's surface; Milrow: 1 million ton, 1969 at 1200 m below surface; and Cannikin: 5 million-ton, 1971 at 1763 m below surface (the world's largest underground test). The Department of Energy has conducted monitoring of this site for a number of years and has found little evidence of radionuclide leakage (Sibley and Tornberg, 1982; Burger et al., 2006). We collected a suite of fish samples from areas adjoining Amchitka and tested it for natural and anthropogenic radionuclides. In this report, we report the concentration of gamma-emitting radionuclides (^{40}K , ^{137}Cs , ^{226}Ra , and ^{226}Ra) from a suite of fish samples that we obtained from our collaborators.

2. Materials Methods:

The fish samples were donated to the project by Joanna Burger of Rutgers University and John Kelley and Doug Dasher, University of Alaska. These fish samples were collected from various locations in 2004 and summer of 2006 and those that were collected in 2004 were archived immediately after collection. The flesh of fish samples were dried at 60°C for 72 hours. From the dry and wet weights, the weight loss was calculated. A known amount of dried sample was then ashed at 550°C. A known weight of the ash was packed into a 10-ml counting vial and assayed for gamma-emitting radionuclides. Typically, the samples were counted for 24-36 h, depending on the activities of various gamma-emitting radionuclides. There was no peak background in any of the radionuclides analyzed, except for ^{40}K for which the background corrections were made.

For ^{210}Po determination, a known amount of dried sample was digested in conc. HNO_3 and HCl , after adding a known amount of ^{209}Po as yield tracer. Details are given in Baskaran and Naidu (1995).

The concentrations of ^{137}Cs , ^{226}Ra , ^{228}Ra , and ^{40}K were determined using a high-purity, germanium Well-Detector coupled to a Canberra InSpector multichannel analyzer. The gamma ray detector was calibrated with sediment standards for those gamma energies that were used for determining the concentrations of radionuclides. The standards utilized were obtained from the International Atomic Energy Agency (IAEA). These standards include IAEA-300 for ^{137}Cs (661.6 keV), RGU-1 for ^{210}Pb (46.5 keV), and ^{226}Ra (via ^{214}Pb , 352 keV and 609 keV), RGTh-1 for ^{228}Ra (via ^{228}Ac , 338 and 911 keV), and RGK-1 for ^{40}K (1460.8 keV). The standards were calibrated for various geometries. In the case of ^{226}Ra , the powdered sample was packed in the counting vial and stored for about 4 weeks for the growth of ^{222}Rn and its daughter products to reach secular equilibrium with its parent, ^{226}Ra . Typical resolution (full-width at half-maximum) was about 1.3 keV at 46 keV and 2.2 keV at 1.33 MeV. The peak/Compton ratio for ^{60}Co (1332 keV) was 45.0:1. Peak analysis was performed with the software

peak analysis that came with the InSpecor (Canberra Company). ^{210}Pb activities were not specifically corrected for self-absorption. The matrix densities of the standard and sample are quite comparable, and the self-absorption corrections were not applied for both the standard and the samples. In the past, we had measured ^{210}Pb concentrations in selected sediment samples by alpha counting of its daughter, ^{210}Po , and compared the activities obtained by alpha counting with the gamma counting. It was found that no self-absorption corrections were necessary when the standard used for calibration (dpm/cpm ratios for standards for various geometries), and the sample has comparable densities.

3. Results and Discussion:

The concentrations of measured radionuclides are given in Table 1 (attached herewith). The concentrations of ^{134}Cs , ^{60}Cs and ^{234}Th were all below detection limit in all of the analyzed samples. Of the remaining gamma-emitting radionuclides, ^{40}K and ^{137}Cs are the most abundant ones. In the three major fish groups (Rockfish, Scullion, and Brock), the concentrations in Scullion varied between below detection limit to 140 mBq/kg (wet weight), with a mean value of 119.3 mBq/kg. The corresponding values in the Rock fish are lower (range: below detection limit to 225 mBq/kg, with a mean value of 85.2 mBq/kg). The concentration in the Brock samples is comparable to that found in Scullion, with a mean value of 115.7 mBq/kg. Our observation is similar to the observation reported by Burger et al. (2001) in which they reported widely varying concentrations of ^{137}Cs among fish species inhabiting the same environment, and fish from a known-contaminated site had ^{137}Cs levels an order of magnitude above the reference site. The data from the CRESP Amchitka/Kiska study also indicates differences among species in ^{137}Cs . However, the levels of ^{137}Cs are well below any food safety guidelines (U.S. Food and Drug Administration derived intervention level for radioactivity in food is 1,200 Bq/kg), and they are most likely derived from global fallout. The main contribution of Cs-137 was global fallout from above ground nuclear tests, which contributed a more or less uniform ‘blanket’ (although varying with latitude and amount of precipitation at any given location) of fallout. For all species of fish, the mean Cs-137 levels in the present study were below those reported prior to 1975 (which was after the nuclear test shots on Amchitka) and this is attributed to the lack of additional source input to counter balance the decrease due to radioactive decay (half-life = 30 yrs).

The data obtained for this investigation can be compared to the 2004 CRESP data from the same fish species as well as other species. Overall, the activities of ^{137}Cs and other radionuclides were all well below 1,200 Bq/kg (U.S. FDA’s intervention level for radioactivity) and thus provides added assurance of environmental health with respect to fish, and consumers of these fish.

Comparison of Cs-137 levels (Bq/kg wet weight) in fish

Species	1967-'68	'65-'75	2004 (CRESP)	Present data
Rock Greenling	0.89 (100)	0.523 ^E	<MDA ^F	0.085
Walleye Pollock				
Halibut	1.24 (50)	0.58 ^E	0.14 (75)	
Pacific Cod				
Scullion				0.12

E: Percent above MDA not given; F: mean MDA for the CRESF study was 0.29 which is below the mean value reported prior to 1975.

Our ^{137}Cs concentrations also can be compared to the average concentration in Irish Sea is 4.64 Bq/kg (wet wt); range: 0.31-13 Bq/kg; other sites: average: 0.22 Bq/kg; range: 0.04-0.33 Bq/kg; CRESF: average: 0.04-0.31 Bq/kg; range: 0.09-0.60 Bq/kg. Thus, our concentration range of 33 to 225 mBq/kg is lower than the values reported in the 2004 study.

The concentration of ^{40}K remains more or less the same in all species, between 39 and 79.9 Bq/kg. The mean values for each group does not vary considerably. Measurable concentrations of ^{228}Ra were found in only about 1/6 of the samples analyzed. Radium-226 concentrations vary almost by a factor of 2 within these three groups of fish. The mean values of Ra-226 for each group of fish are listed in Table 1. In particular, ^{137}Cs is distributed throughout the soft tissue of the fish and other organisms. In most of the samples, the time elapsed between sampling and analysis was long that most of the in-situ ^{210}Po has decayed away and hence the ^{210}Po activities in those samples represent the activities of its parent, ^{210}Pb . However, on a few fresh samples that were collected in the summer of 2006, the activities of in-situ ^{210}Po is relatively high (as high as 1.79 Bq/kg). It is known that ^{210}Po is the largest contributor to the radiation dose in marine organisms (Cherry and Heyraud, 1982). Thus, it is not surprising that the radiation level of in-situ ^{210}Po is significantly higher than that of ^{137}Cs .

4. Radiation Dose Estimate:

- From the concentration of radionuclides, the intake of these nuclides can be calculated by multiplying the activity (Bq/kg) and the amount of fish consumed in a year (kg/year). For adults, it is recommended that generic annual ingestion rate of 50 kg/a of fish and 15 kg/a of shellfish be used (IAEA, 2003). Dose per unit activity concentration coefficients reported in Table 1 have been calculated assuming that the ingestion rate of shellfish is equally divided between crustaceans and mollusks. For infants aged 1 to 2 years, an annual consumption rate of 25 kg/a of fish should be used. The total annual effective dose from the ingestion of seafood, $E_{\text{ing,food,public}}$ (in Sv/a), can be calculated using the equation

$$E_{\text{ing,food,public}} = \sum H_B(k) \sum (C_B(j,k) DC_{\text{ing},j}(j)) \quad (1)$$

where $H_B(k)$: rate of human consumption of seafood k (in kg/a)

$DC_{\text{ing},j}(j)$: dose coefficient for ingestion of radionuclide j (in Sv/Bq)

$C_B(j,k)$: concentration of radionuclide j in the edible fraction of seafood k (in Bq/kg fresh weight).

Using a internal dose coefficient of 1.3×10^{-8} Sv/Bq for ^{137}Cs , the calculated dose from ^{137}Cs ranges from 5.5×10^{-8} Sv/yr to 8.3×10^{-8} Sv/yr. Comparing this value to the DOE radiation dose limit for public of 1.0×10^{-3} Sv/yr (= 1mSv/yr), the ^{137}Cs present do not pose any health threat. Including all the other naturally-occurring radionuclides reported in this study, the total radiation dose received from the ingestion of seafood is negligible and hence do not pose any threat to humans. The internal dose coefficient for other measured radionuclides are: Ra-226: 2.8×10^{-7} Sv/Bq; Pb-210: 6.9×10^{-7} Sv/Bq; ^{210}Po : 1.2×10^{-6} Sv/Bq; IAEA, 2003)

5. Recommendations for Future Studies:

Polonium-210 contributes the highest radiation dose in biological organisms in marine systems and thus, timely measurement of Po-210 to assess radiation level is critical. With the highest value of the coefficient for ingestion of radionuclide (1.2×10^{-6} Sv/Bq; IAEA, 2003), and with very high concentration factor (bioaccumulation in food chain), ^{210}Po could possibly pose some threat and hence the concentration of ^{210}Po should be measured. With its 138 days half-life, the analysis should be conducted as quickly as possible. Generally, the gamma-emitting radionuclides levels are low and they do not appear to pose any threat to the people who ingest fish from this region.

6. Quality Control for Radionuclide Analysis:

A multi-level quality control program was employed for radionuclides that included the following components:

- 1) Blind analysis: The coding used for each sample did not identify the source location of the sample or the specific species of the sample.
- 2) We periodically run blind standard samples (Baltic sea sediments, RGU-1 and RGTh-1 standards) was run and the values agreed within 2 standard deviations based on the propagated error arising from counting statistics, background, error in the calibration of the gamma-ray spectrometer and error associated with the certified reference material.
- 3) For Po-210 measurement that requires complete digestion and chemical processing, separate isotopic spike (^{209}Po as internal standard) of known activity was added to verify the recovery. This was done in addition to the blind quality control samples.
- 4) For gamma counting, instrumentation calibration was checked periodically using International Atomic Energy Agency's Certified Reference Standards (RGU-1 for Ra-226, Pb-210; RGTh-1 for Ra-228; Baltic Sea Sediments for Cs-137 and RGK-1 for K-40). There was no peak background in any of the U-Th series radionuclides. However, ^{40}K had a relatively small background and all the samples were corrected for this peak background. Geometric calibration for each of the gamma energy was carried out using independent certified reference standards, prepared by us to match the geometry of the specific sample in the gamma counting vial and density of the sample was also taken into consideration.
- 5) Each of the gamma-ray spectrum was independently reviewed to make sure the software (developed and provided by CANBERRA Inc.) utilized in the spectrum analysis is correct.
- 6) All analytical results reported with the uncertainty for each sample. The uncertainty is the 1-sigma propagated error arising from counting statistics, background subtraction, and the error associated with the calibration of the instrument.
- 7) We periodically participate in inter-calibration exercise with other agencies (such as U.S. Geological Survey, Scripps Institution of Oceanography, NIST, etc).

7. **References:**

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Appendix-A: Standard Operating Procedure for Using the Genie-PC Gamma Spectroscopy System (Ge-well detector)

- 1.0 Location
Room 225 Life Science Bldg., Wayne State University
- 2.0 Purpose
This system will qualitatively and quantitatively determine gamma-emitting radiation.
- 3.0 Applicability
This system will detect any gamma rays in the sample (environmental as well as high activity samples).
- 4.0 References
Genie-PC Basic Operation – Canberra
- 5.0 Discussion
A standard of the same geometry as the sample, and of known activity must be measured to quantitatively determine the radionuclide concentration. Determination of the ratios of disintegration per minute to counts per minute (dpm/cpm for each geometry--see Figure 1) as well as an energy calibration is necessary. For qualitative determination, an energy calibration is the only one needed.

6.0 Liquid Nitrogen Procedure

- 6.1 Stop the detector
- 6.2 Open the pressure release valve (silver knob) on the large nitrogen tank. Release the pressure until it falls to 100psi (or below). Close pressure valve.
- 6.3 Begin filling the liquid nitrogen dewar by opening the liquid valve (blue knob). This must be filled once every 3-4 days (for a germanium detector).
- 6.4 Filling is complete when the LN₂ begins to fall to the floor. After filling is complete, restart the acquisition.
- 6.5 About every six fills (of the dewar) the large liquid nitrogen tank will need to be refilled. To do this:
 - 6.5.1 Stop the detector
 - 6.5.2 Disconnect the hose from the tank.
 - 6.5.3 Go to the Sci. Store and pick up the key for the liquid nitrogen tank (nitrogen is located outside, in between the Science and Life Science bldgs.). Also pick up the dolly for the big tank.
 - 6.5.4 Load the tank onto the dolly and take it outside for re-filling.
 - 6.5.5 Connect the tank to the hose for re-filling LN₂.

- 6.5.6 Open the pressure valve (silver knob) all of the way, open the liquid valve (blue knob) all of the way, then open the LN₂ all of the way
- 6.5.7 When filling is complete (LN₂ is falling to the ground, you will also hear a change in the sound) close the valves in the opposite order that they were opened (LN₂ knob first, then close the liquid valve, then close the pressure valve)
- 6.5.8 Bring tank back to the lab and reconnect to the dewar
- 6.5.9 Restart the detector
- 6.5.10 Return the key and dolly to the Sci. Store

7.0 Sample Counting Procedure

- 7.1 To open the prgm: Double click on Gamma Acquisition and Analysis icon.
- 7.2 Click on File, Click on Open Datasource
- 7.3 Select the datasource type by clicking on the circle for Detector (as opposed to Cam File), Under inputs select DET 01, click OK
- 7.4 Carefully open the gamma detector and load the sample (be sure to write the sample info in the gamma-log notebook before putting the sample into the detector)
- 7.5 Select Edit, Select Sample Info and fill in the required fields
 - 7.5.1 For sample title: fill in the sample id and sample weight
 - 7.5.2 Type in your initials under collector name
 - 7.5.3 In the right hand column, fill in the sample id
 - 7.5.4 Also on the right, fill in the sample geometry
 - 7.5.5 Click OK once you've filled in the required fields
- 7.6 Click on START. This will start the gamma detector.

8.0 Changing the Sample

- 8.1 Click on STOP
- 8.2 Click on File, click on Save as, type in the file name (up to eight characters.cnf), Be sure to write down the name the sample has been saved as in the gamma-log notebook, Click on OK
- 8.3 Click on the trash icon, Click on Analyze, Click on Execute sequence, once the trash icon is re-enabled, click on the print icon.
 - 8.3.1 Label the printout with the name that the file was saved as in the top right corner.
 - 8.3.2 Mark the peaks of interest (see Figure 2)
- 8.4 Click on CLEAR
- 8.5 Change the sample in the detector (write down new sample info in the gamma-log notebook)
- 8.6 Mark the counted sample with a small dot at the top so that we know it has been counted
- 8.7 Change the sample info in the computer (see step 7.5)
- 8.8 Click on START. This will start the gamma detector.

9.0 Changing the power source

- 9.1 Before the power on the gamma detector is turned off, the voltage must be decreased (see 10.1.2.1). Failure to do so could result in damage to the detector! To decrease the voltage:
 - 9.1.1 Click on MCA, Click on Adjust, Choose HPVS (high power voltage source) in the top of the box, then reduce the voltage with the slide scale. Once the voltage is reduced, turn it off by clicking OFF, close window.
 - 9.1.2 It is now safe to turn the power off on the detector.
 - 9.1.2.1 Often when the power source needs to be replaced, it is due to power failure. When this is the case, there is no need to turn down the voltage as it is already off.
 - 9.1.3 Replace the power source
 - 9.1.4 Once power has been restored, open the genie software (see 7.1-7.3)
 - 9.1.5 Click on MCA, Click on Adjust, Choose HPVS in the top of the box, Click ON (at this stage the computer should ask you to wait while the voltage revs up), increase the voltage to 4000V, Click OK, Click on EXIT.
 - 9.1.6 The detector is ready to count samples (refer to steps 7.4-7.6).

Appendix-B: Standard Operating Procedure for Using the EG &G ORTEC, Octete PC Alpha Spectrometer

- 10.0 Location
Room 225 Life Science Bldg., Wayne State University
- 11.0 Purpose
This system will quantitatively determine alpha-emitting radiation.
- 12.0 Applicability
This system will detect alpha emitting isotopes in the sample (environmental as well as high activity samples).
- 13.0 Software
Maestro for Windows
- 14.0 Discussion
The basic alpha spectroscopy system consists of an alpha spectrometer (vacuum chamber and amplifier electronics), eight alpha detectors, analog to digital converter (ADC), multi-channel analyzer (MCA), computer software, and printer. Plated (electroplated or chemically plated) samples are placed on the sample holder in the alpha spectrometer and a vacuum is pulled on the spectrometer vacuum chamber. As alpha particles are emitted from the sample, the alpha detectors produce electronic signals that are analyzed by the MCA to generate a digital spectrum that is equivalent to the energy of the alpha particles. The spectrum is then analyzed by computer software (Maestro for Windows), which identifies and quantifies the alpha energies.
- 15.0 Procedure
- 15.1 To Open Program**
- 15.1.1 Click on START, Click on PROGRAMS, Click on MAESTRO 32,
Click on MAESTRO for Windows
- 15.2 To Change Samples**
- 15.2.1 **Stop each detector:** Click on AQUIRE, Click on STOP
- 15.2.1.1 This must be done for each detector individually.
To switch from detector to detector, click on the detector icon in the top right corner.
- 15.2.2 **Turn off the bias on each detector:** Click on AQUIRE, Click on ADJUST CONTROLS, Click on OFF, Click on OK

- 15.2.2.1 This must be done for each detector individually.
To switch from detector to detector, click on the detector icon in the top right corner.
- 15.2.3 **Save the file:** Click on FILE, Click on SAVE AS, Choose a file name. There is no character limitation, but each file name must end in ---.CHN
- 15.2.4 **Record the file name in the alpha-log notebook** (red notebook) as well as the date and time that the sample was changed
- 15.2.5 **To mark the peaks of interest, first clear the ROI** (regions of interest): Click on ROI, Click on CLEAR ALL, Then mark the peaks of interest by clicking F2. This will allow you to mark and unmark the peaks.
- 15.2.6 **Save these peaks of interest and take a printout:** Click on FILE, Click on SAVE, Click on ROI REPORT.
- 15.2.6.1 If you want to print the entire spectrum (not just the ROI), Click on PRINT rather than ROI REPORT.
- 15.2.7 **Clear the spectrum:** Click on ACQUIRE, Click on CLEAR
- 15.2.8 **Change the sample:** Vent the detector by slowly turning the knob to the left. Open the detector and change the sample. Place the sample that was just counted into its respective sample bag. Close the detector and slowly turn the knob back to the right.
- 15.2.9 **Edit the sample info** (for the new sample): Click on SERVICES, Click on SAMPLE DESCRIPTION: Type in the sample ID, the sample weight, the amount of spike added, and the date the sample was plated, as well as any other pertinent information.
- 15.2.10 REPEAT STEPS 6.2.3-6.2.9 UNTIL ALL SAMPLES ARE CHANGED**
- 15.2.11 **Turn on the bias on each detector:** Click on ACQUIRE, Click on ADJUST CONTROLS, Once the vacuum is below 300 mT, Click ON, Click OK

15.2.11.1 This must be done for each detector individually.

To switch from detector to detector, click on the detector icon in the top right corner.

15.2.12 **Start each detector:** Click on ACQUIRE, Click on START

15.2.13 **To recall saved files:** In the top right corner switch from DET # to Buffer. Click on FILE, Click RECALL, Choose the folder, then file name to be opened, Click OPEN

15.2.14 **To return to the counting screen:** In the top right corner switch from Buffer to DET #.

Figure 1: Calibration for dpm/cpm ratios for Detector #1

	Pb-210		Th-234		Ra-226		Ra-226		Ra-228		Ra-228		Cs-137		Be-7	
geom	46 KeV		63 KeV		352 KeV		609 KeV		338 KeV		911 KeV		661 KeV		476 KeV	
(ml)	dpm/cpm	Error														
1	36.25	0.49	42.94	0.70	8.90	0.06	24.88	0.23	30.97	0.73	39.09	0.94	6.97	0.11	43.83	0.49
2	38.26	0.42	41.88	0.53	9.16	0.06	25.25	0.19	34.11	0.77	43.82	1.00	7.44	0.11	44.98	0.45
3	41.87	0.45	47.30	0.60	10.57	0.07	27.52	0.21	35.26	0.74	44.29	0.93	8.43	0.06	51.24	0.51
4	47.96	0.48	52.64	0.59	11.80	0.07	29.44	0.21	40.05	0.84	50.34	1.06	9.27	0.12	56.66	0.54
5	52.11	0.48	53.04	0.51	12.41	0.07	30.75	0.20	49.72	1.04	61.89	1.30	10.85	0.11	59.50	0.55
6	62.75	0.58	65.52	0.67	14.20	0.08	33.64	0.22	48.35	1.08	59.98	1.35	12.43	0.09	67.36	0.61
7	73.01	0.67	77.46	0.79	16.23	0.09	37.75	0.24	53.78	1.12	65.70	1.37	14.57	0.1	76.62	0.69
8	84.37	0.65	87.83	0.75	18.63	0.10	42.17	0.25	63.03	1.30	75.82	1.57	15.95	0.11	87.39	0.75
9	90.53	0.81	94.70	0.91	19.90	0.11	44.71	0.28	70.90	1.47	85.92	1.78	17.76	0.11	93.16	0.82
10	103.12	1.04	111.03	1.28	22.55	0.13	49.90	0.33	84.88	1.76	101.94	2.11	19.62	0.17	105.14	0.97

Figure 2: Gamma emitters in the Environment by energy (peaks of interest)

Nuclide	Energy (keV)	Intensity (%)
Pb-210	46.5	4.0
Th-234	63.0	3.5
Ra-228 (via Ac-228)	338.5	12.3
Ra-226 (via Pb-214)	352.0	35.0
Be-7	477.6	10.8
Ra-226 (via Bi-214)	609.4	43.0
Cs-137	661.6	85.1
Ra-228 (via Ac-228)	911.1	29.0